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Journal

Journal of Geophysical Research Atmospheres, 101(D2)

ISSN

0148-0227

Authors

Blake, DR
Blake, NJ
Smith, TW
et al.

Publication Date

1996

DOI

10.1029/95JD01370

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Nonmethane hydrocarbon and halocarbon distributions during Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange, June 1992

Donald R. Blake, Nicola J. Blake, Tyrrel W. Smith Jr.¹, Oliver W. Wingenter, and F. Sherwood Rowland

Department of Chemistry, University of California, Irvine.

Abstract. Aircraft measurements of selected nonmethane hydrocarbon and halocarbon species were made in the lower troposphere of the NE Atlantic near the Azores, Portugal, during June 1992 as part of the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange. In this paper, the impact of continental outflow from both Europe and North America on the study region were assessed. Four main air mass types were characterized from trajectories and trace gas concentrations: clean marine from the Atlantic, and continental air from the Iberian Peninsula, the British Isles and Northern Europe, and North America. Each classification exhibited trace gas concentrations that had been modified en route by photochemical processes and mixing. Comparison with the clean marine boundary layer (MBL) shows that the boundary layer of the predominantly continental air masses were enhanced in hydrocarbons and halocarbons by factors of approximately 2 for ethane, 5 for propane, 2-6 for ethyne and benzene, and 2-3 for C₂Cl₄. The same air masses also exhibited large ozone enhancements, with 2 to 3 times higher mixing ratios in the continental boundary layer air compared to the clean MBL. This indicates a primarily anthropogenic photochemical source for a significant fraction of the lower tropospheric ozone in this region. Methyl bromide exhibited on average 10-20% higher concentrations in the boundary layer affected by continental outflow than in the clean MBL, and was seen to be enhanced in individual plumes of air of continental origin. This is consistent with significant anthropogenic sources for methyl bromide. In addition, median MBL concentrations of ethene and methyl iodide showed enhancements of approximately a factor of 2 above free tropospheric values, suggesting primarily coastal/oceanic sources for these species.

Introduction

Nonmethane hydrocarbons (NMHCs) and halocarbons can play critical roles in tropospheric chemistry, and many of the halocarbons are important as infrared absorbers of terrestrial radiation and are halogen sources to the stratosphere. Anthropogenically produced halocarbons are released predominantly in urban areas and may be used to estimate the recent anthropogenic influence of an air parcel [Blake *et al.*, 1992, 1994, 1995; Smith, 1993]. The concentrations of selected chlorofluorocarbons (CFCs) and other halocarbons have been published for Ireland [Prinn *et al.*, 1983; Simmonds *et al.*, 1993] and for the Pacific [Elkins *et al.*, 1993; Wang, 1993]. The variation of tetrachloroethene in the Pacific has been characterized by Wang *et al.* [1995], and in the North Atlantic for tetrachloroethene and methyl chloride by Koppmann *et al.* [1993]. NMHCs are emitted from a variety of biogenic and anthropogenic sources and may be used to distinguish fossil fuel leakage, biomass burning, industrial activity, and natural gas

emissions [Singh and Zimmerman, 1992; Blake *et al.*, 1994, 1995]. The measurement of a variety of NMHCs and halocarbons, which have atmospheric lifetimes ranging from days to hundreds of years, can be used to study the history of an air mass and to verify model-based trajectories.

The eventual atmospheric destruction of many of these gases is dependent on photochemistry that can lead to O₃ formation. Atmospheric ozone photolyzes in the troposphere to form O(¹D) atoms, which in turn, can react with H₂O to produce hydroxyl (HO) radicals. Oxidation by HO radicals is the primary process for removal from the atmosphere for most NMHCs and for the halocarbons with carbon-carbon double bonds or abstractable hydrogen. The residual radicals left after reaction with HO radicals are subsequently involved in various radical propagation mechanisms, including reaction with nitrogen radicals NO and NO₂, collectively described as NO_x. When NO_x mixing ratios exceed about 200 parts per trillion by volume (pptv), these successive reactions tend to increase the amount of ozone present, while maintaining high levels of both HO and NO_x. In contrast, in the near absence of NO_x, frequently the case in clean maritime air, the reaction sequences tend to reduce the concentrations of both O₃ and HO. Alternatively, ozone can react directly with hydrocarbons containing carbon-carbon double bonds. In addition, ozone has been postulated to react with sea salt to produce Cl radicals [Graedel and Keene *et al.*, 1995], another powerful oxidant that is discussed by Wingenter *et al.* [this issue]. For each initial molecular type, the reaction

¹ Now at National Center for Atmospheric Research, Boulder, Colorado.

rates and mechanisms are different, but each may be responsible under high NO_x conditions for the eventual production of several O_3 molecules [e.g., *Hough and Derwent*, 1987]. Therefore, ozone is of central atmospheric importance as a major oxidant itself, but also because its photolysis can play a central role in initiating the photochemical production of other key oxidizing species. Insight into the distribution of tropospheric O_3 and its precursors, and to the processes that control their production and removal, is essential to understanding the oxidative capacity of the troposphere.

Both Europe and North America are known to be large sources of photochemical pollutants and precursors for the North Atlantic region. Satellite and space shuttle measurements [Fishman *et al.*, 1990; Reichle *et al.*, 1990] have revealed elevated summertime concentrations of the pollutants ozone and CO from North American emissions that have been transported clockwise around the North Atlantic subtropical (Azorean) high between the United States and Europe. Several measurements of NMHCs have been made in the North Atlantic [Rudolf and Ehhalt, 1981; Cofer, 1982; Van Valin and Luria, 1988; Rudolph and Johnen, 1990; Koppmann *et al.*, 1992], but very few are available for the summer months. Many measurements of NMHCs have also been made in the remote marine atmosphere of the Pacific [e.g., Singh and Salas, 1982; Greenberg and Zimmerman, 1984; Bonsang and Lambert, 1985; Singh *et al.*, 1988; Blake *et al.*, 1995]. Most NMHCs show a great deal of variability, and several papers have related NMHC concentrations to transport times from the North American and European continents [e.g., Van Valin and Luria, 1988; Koppmann *et al.*, 1992; Parrish *et al.*, 1992].

Studies have shown that seawater, usually in coastal regions, can be supersaturated in methyl iodide [Moore and Tokarczyk, 1993]. Methyl iodide has an approximately 5-day atmospheric lifetime against photolysis [Zafiriou, 1974], long enough for oceanic emissions to be extensively mixed into the lower

troposphere. Methyl iodide has been suggested as the main carrier of iodine from the ocean to the atmosphere [Lovelock *et al.*, 1973].

During June 1992, the Marine Aerosol and Gas Exchange (MAGE) atmospheric chemistry component of the Atlantic Stratocumulus Transition Experiment (ASTEX) was conducted in the central and eastern regions of the North Atlantic Ocean. The general area of study for ASTEX/MAGE was contained in a triangle located in the eastern North Atlantic, with vertices extending southeast from Santa Maria Island (37.0°N, 25.1°W), to Porto Santo (33.1°N, 16.3°W) in the Madeira Islands, and to an open ocean point (27.5°N, 24.0°W) marked by a navigational buoy. The sampling locations are illustrated in Figure 1 (see also Huebert *et al.* [this issue]). Because of the major airfield at Santa Maria Island, it served as the base for most of the aircraft involved in ASTEX/MAGE. The National Center for Atmospheric Research (NCAR) Electra aircraft was the main sampling platform used for collection of the whole air samples discussed in this paper. The other research aircraft operating in this region during ASTEX/MAGE included the University of Washington C-131, the United Kingdom Meteorological Office C-130, and the French Meteorological Merlin IV and Folker 27. Data collected during flights of the aircraft allowed for characterization of the tropospheric distribution and variability of chemical species, as well as assessment of the local and long-range transport of natural and anthropogenic emissions to the study region. Ground samples were collected on Santa Maria Island and on the larger São Miguel Island (37.7°N, 25.5°W), 60 mi (100 km) north of Santa Maria. The focus of this paper is the description of the distributions of several C_2 - C_7 NMHCs and C_1 - C_2 halocarbons measured in the canisters collected on the NCAR Electra or on local islands. An accompanying paper describes the use of these NMHC and halocarbon data in a Lagrangian experiment to determine atmospheric hydroxyl, atomic chlorine and vertical mixing [Wingenter *et al.*, this issue].

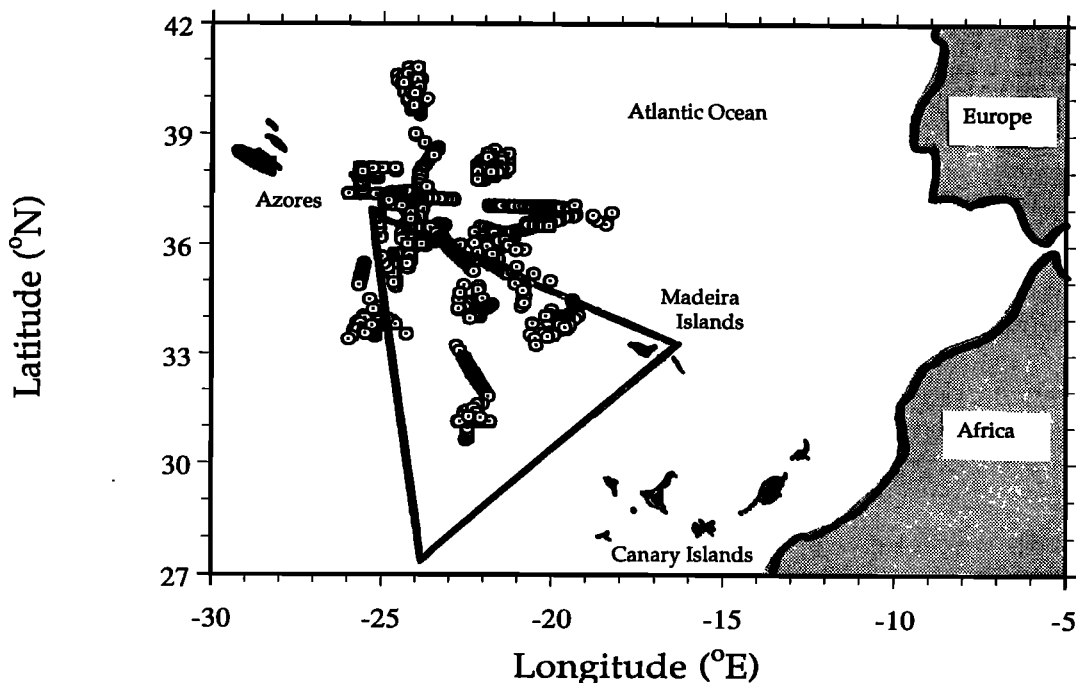


Figure 1. Locations of all aircraft whole air samples collected during ASTEX/MAGE.

Experiment

During the 4-week intensive study, 808 whole air samples were collected in individual evacuated air canisters, and subsequently assayed for selected halocarbons and NMHCs. Of these 808 samples, 634 were collected onboard the NCAR Electra by members of the University of California, Irvine (UCI) research group. The aircraft samples were pressurized primarily to ensure that sufficient air was collected at higher altitudes. One hundred seventy samples were collected at various surface locations, including aboard the NOAA R/V *Oceanus* and R/V *Malcolm Baldrige* (24 and 48 samples, respectively). Sampling on Santa Maria and São Miguel Islands in the Azores accounted for 64 and 20 samples, respectively. The remaining 18 samples were collected in the exhaust of various aircraft participating in ASTEX/MAGE prior to their taking off from Santa Maria Island. Complete details of the air canister fabrication, sample filling procedures, and trace gas chemical analyses have been described elsewhere [Blake *et al.*, 1992, 1994, 1995; Smith, 1993]. Brief descriptions of the sample filling procedure and chemical analysis follow. Some changes were made to the exact chromatographic analytical procedures used in ASTEX/MAGE from those applied during the immediately preceding NASA aircraft experiments of the Pacific Exploratory Mission (PEM West-A) [Blake *et al.*, 1995] and the Airborne Arctic Stratospheric Experiment (AASE II).

Sample Filling Procedure

Two-liter stainless steel canisters were assembled in fixed sets of 24, interconnected in series. On the Electra, a rack mounting was fabricated to contain three of these 24-canister sets, allowing a maximum of 72 samples to be collected per flight. One week prior to the commencement of ASTEX, the canisters were evacuated to a pressure of 10^{-2} torr and shipped via air cargo to Santa Maria Island. After conclusion of the flights, the canisters were sent for analysis to a temporary laboratory established by our research group at the NOAA Atlantic Oceanographic Meteorological Laboratory in Key Biscayne, Florida. The location of this laboratory was dictated by the logistical requirements of the NASA TRansport and Chemistry near the Equator (TRACE-A) project which came immediately after the conclusion of ASTEX/MAGE. The laboratory was in operation from July through November 1992.

Outside air was brought into the NCAR Electra through a 1/4-inch stainless steel inlet mounted on the port side of the fuselage just before the wing, and extended out 12 inches, sufficient to reach beyond the laminar boundary layer of the aircraft. This inlet was attached in series to a mass flow controller (Brooks Instrument Division, model 5850 E series), a two-stage metal bellows pump (Metal Bellows Co., MB-602), and a gas-handling manifold. The manifold was mounted on the base of the rack and directed the air flow to each of the three 24-canister sets. Air was continuously pumped through the manifold to flush the inlet lines and canister tubing before exiting the aircraft through an outlet mounted directly behind the inlet. This configuration allowed the system to be operated from subambient pressures to 45 psig, above which a pressure relief valve was activated. Depending on the mass flow controller setting and the ambient pressure associated with a particular altitude, the time required to pressurize a sample to 40 psig ranged from 10 to 120 s. Therefore, depending on the speed and the ascent/descent rate of the Electra, each sample represents an air mass sampled over a horizontal distance of 0.7 to 10 km or a vertical distance of up to 300 m.

Chemical Analysis

Each whole air sample was analyzed for NMHCs and halocarbons using a trace gas apparatus with three gas chromatographic separation columns contained in two temperature programmed Hewlett-Packard 5890 Series II gas chromatographs. Four separate gas chromatograms were obtained for each sample. Exactly 700.0 ± 0.1 torr of air were transferred from an air canister to a 2-L stainless steel storage vessel fixed permanently to the vacuum line. The condensable trace gases were trapped on a preconcentration loop (10 inch x 1/4 inch OD stainless steel) filled with 1-mm-diameter glass beads and immersed in liquid nitrogen. After 600.0 torr of sample from the storage vessel and vacuum line (equivalent to 1520 cm^3 at STP) had passed through the preconcentration trap, the loop and its contents were isolated via a 1/8-inch UWP six-port switching valve (Valco Instruments, Houston, Texas) and heated with hot water (80°C) to revolatilize the gases. The H_2 carrier was redirected to flush the contents from the loop to the splitter, which partitioned the gas flow to the three different columns.

The first gas chromatograph (GC-1) was equipped with a flame ionization detector (FID) and an electron capture detector (ECD), while the second gas chromatograph (GC-2) was equipped with two FIDs. Installed in GC-1 was a 60 m x 0.25 mm DB-1 column (J & W Scientific). The effluent from this DB-1 column was split with 2.2 ml/min of the carrier flow diverted to the FID to detect C_3 - C_{10} NMHCs, and 2.6 ml/min of the carrier flow directed to the ECD for C_1 - C_2 halocarbon detection. A 30 m x 0.53 mm $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT column (J & W Scientific) with a hydrogen carrier flow of 5.8 ml/min was installed in the FID of GC-2 and separated C_2 - C_5 NMHC compounds. A 30 m x 0.25 mm Cyclodex-B column (J & W Scientific), with a hydrogen carrier flow of 2.2 ml/min was connected to the second FID of GC-2 for C_6 - C_{11} NMHC analysis.

The PLOT, DB-1, and Cyclodex columns have unique separation characteristics, therefore the elution order of the hydrocarbons on each is quite different, and any coelution of gases on one column is very likely to be resolved on one of the other columns. This chromatographic technique provided nearly unequivocal peak identification for the C_2 - C_7 NMHCs. The time required for one complete cycle of trapping and injecting a sample was about 24 min. For analysis of ASTEX/MAGE samples, this analytical apparatus was used continuously (24 hours/d, 7 d/week) for a 4-week period prior to Hurricane Andrew, August 24, 1992, and for 3 weeks after September 8, the date the lab was again functional.

To monitor the consistency and reproducibility of the analytical system, a secondary working standard contained in an Aculife treated Luxfer cylinder (dry ambient air collected at Niwot Ridge, Colorado) was analyzed after every four samples. To ensure there was no drift in this working standard, two other whole air cylinders were assayed randomly throughout the project. Concentrations of reported gases in the working standard exhibited no statistically significant changes (1 sigma) in their mixing ratios during 379 measurements over the course of the project.

Because the concentrations for some of the gases in the working standard were significantly higher than those routinely encountered during the missions, our measurement precision for the gases assayed during ASTEX are based on 4 samples collected in the MBL during a 16 minute period of mission 11. The mean mixing ratios, along with the corresponding 1-sigma standard

deviations were (in pptv) ethane 1112 ± 6 ; ethene 43.8 ± 5.9 ; ethyne 298.3 ± 4.7 ; propane 144.0 ± 1.9 ; propene 20.2 ± 2.1 ; n-butane 69.1 ± 1.9 ; i-butane 53.5 ± 1.6 ; n-pentane 11.0 ± 1.0 ; benzene 103.5 ± 3.2 ; and toluene 41.7 ± 2.9 . Propyne and n-hexane were below their 3 pptv detection limit. The mean halocarbon mixing ratios and standard deviations for these samples were (in pptv) CCl_2F_2 (CFC-12) 501 ± 1.0 ; CCl_3F (CFC-11) 269 ± 1.2 ; $\text{CCl}_2\text{FCClF}_2$ (CFC-113) 78.1 ± 0.2 ; $\text{CClF}_2\text{CClF}_2$ (CFC-114) 14.55 ± 0.07 ; CBrF_3 (Halon-1301) 2.21 ± 0.02 ; CBrClF_2 (Halon-1211) 2.33 ± 0.03 ; CH_3CCl_3 (methyl chloroform) 159.2 ± 0.4 ; CHCl_3 (chloroform) 12.4 ± 0.1 ; CCl_4 (carbon tetrachloride) 107.4 ± 0.5 ; C_2Cl_4 (tetrachloroethene) 23.3 ± 0.2 ; CH_3Cl (methyl chloride) 570 ± 5 ; CH_3Br (methyl bromide) 9.8 ± 0.7 ; and CH_3I (methyl iodide) 0.56 ± 0.10 . Because it is highly unlikely that the air mass was completely homogenized, all precision estimates represent upper limits. This is particularly evident for ethene, propene, methyl bromide and methyl iodide, all of which have marine sources.

Results

A total of 634 discrete whole air canister samples were collected in the altitude range of 30 m to 6 km during 15 flights made aboard the NCAR Electra between June 4 and 22, 1992. Most flights contained multiple altitudinal profiles to aid in the characterization of chemical variability of the vertical column. Individual flight information, including sampling periods, predominant origins of air masses from trajectory information, approximate sampling areas, and brief mission descriptions are given in Table 1.

Meteorological descriptions of ASTEX/MAGE can be found in the work of Bretherton and Pincus [1995]. In summary, the flights were conducted near the North Atlantic surface high-pressure system, the center of which was located to the west of the sampling region. This area was associated with very clean maritime air that was sampled during missions 5, 6 and 7. During the early part of the deployment, transport around this system

brought modified (i.e., diluted and photochemically aged) continental air from North America during missions 1, 3, and 4. Mission 2 was conducted nearer the center of the surface high and was mainly influenced by clean marine air. Later (missions 8 to 10), a surface low moving off the coast of Portugal brought European air from the direction of the Iberian Peninsula to the project area. A ridge associated with a high-pressure system then strengthened to produce northeast winds that transported continental air mainly from the British Isles to the area of operation for missions 11–15.

Table 2 shows the minimum, maximum, mean, median, and standard deviation hydrocarbon and halocarbon mixing ratios in pptv for 200 samples collected in the free troposphere (FT) and for 325 collected in the marine boundary layer (MBL). The position of the temperature inversion denoting the boundary between the MBL and the FT was inferred by reference to the vertical temperature and dew point profiles measured onboard the Electra. To minimize the influence of air that had recently been entrained, 109 samples falling within 200 m of the temperature inversion were omitted.

The free tropospheric and boundary layer samples were further categorized by mission. Box distributions of selected halocarbons and hydrocarbons are displayed in Figures 2 and 3. Fewer than 10 samples were assigned to the FT classification for missions 1, 2, 3, 8, and 12. There were more than 10 MBL samples for each mission. Individual profiles of ozone, ethyne, ethene, C_2Cl_4 , CFC-11, CFC-12, CH_3Br , CH_3I , and temperature, versus altitude for mission 10 are given in Figure 4.

Table 2 reveals that several gases known to have mainly urban sources, such as C_2Cl_4 , CH_3CCl_3 , CFC-113, ethyne, and benzene [e.g., Blake *et al.*, 1995], are slightly elevated in the MBL compared to the free troposphere, indicating, on average, stronger urban influence in the marine boundary layer. This is in accord with previous observations made during summer off the U.S. east coast, where advection of continental pollution principally occurred in the MBL [Anderson *et al.*, 1993]. The box distributions in Figures 2 and 3 show that this trend was

Table 1. Nonmethane Hydrocarbon and Halocarbon Sampling Times, Locations, Predominant Marine Boundary Layer (MBL) Air Mass Types, and Brief Flight Descriptions for ASTEX/MAGE, June 1992

Mission	Date	Sampling Time UT	Latitude Range °N	Longitude Range °W	MBL Air Mass Type	Description
1	June 4	1000-1525	36.1–33.3	23.5–19.6	Modified N American	Cloud transition
2	June 5	1201-1700	36.6–34.9	25.1–24.0	Clean marine	Cloud transition
3	June 8	1148-1647	38.1–37.4	26.9–23.9	Modified N American	Saõ Miguel Island wake effects
4	June 10	0517-1007	36.5–33.8	24.0–19.2	Modified N American	Diurnal variation
5	June 12	1708-2056	40.8–39.5	24.6–23.7	Clean marine	1st Flight of 1st Lagrangian experiment
6	June 13	0439-1021	37.4–35.4	24.4–23.2	Clean marine	2nd Flight of 1st Lagrangian experiment
7	June 13	1616-2114	35.5–33.4	26.0–24.3	Clean marine	3rd Flight of 1st Lagrangian experiment
8	June 15	1148-1552	35.6–33.7	25.5–20.8	Clean marine and continental	Air mass transition - clean marine and continental outflow
9	June 16	1241-1818	37.5–36.6	24.9–18.4	Clean marine and continental	Air mass transition - clean marine and continental outflow
10	June 17	0835-1245	39.0–36.9	25.0–23.4	Clean marine and continental	Air mass transition - clean marine and continental outflow
11	June 18	2217-0333	38.6–37.6	23.7–21.3	Modified continental	1st Flight of 2nd Lagrangian experiment
12	June 19	1040-1600	36.5–35.6	22.3–20.8	Modified continental	2nd Flight of 2nd Lagrangian experiment
13	June 19	2215-0122	36.7–34.0	24.2–21.8	Modified continental	3rd Flight of 2nd Lagrangian experiment
14	June 20	1053-0000	33.2–30.7	22.8–21.8	Modified continental	4th Flight of 2nd Lagrangian experiment
15	June 22	1126-1453	37.1–36.4	21.2–18.3	Modified continental	Haloalkane flux run

Table 2. Comparison of Free Troposphere (FT) and Marine Boundary Layer (MBL) Mixing Ratios for ASTEX/MAGE, June 1992

Compound	Minimum, pptv		Maximum, pptv		Mean, pptv		Median, pptv		s. d.	
	FT	MBL	FT	MBL	FT	MBL	FT	MBL	FT	MBL
Ozone (ppbv)	16	38	90	47	48	38	48	42	16	6
CF ₃ Br	1.9	1.9	3.2	2.5	2.1	2.1	2.1	2.1	0.1	0.1
CF ₂ ClBr	2.7	2.6	3.8	3.8	3.0	3.1	2.0	3.3	0.3	0.4
CFC-12	504	503	577	541	512	512	511	511	7	5
CFC-114	14.6	14.6	17.4	17.1	15.3	15.3	15.3	15.3	0.3	0.3
CFC-11	260	262	303	287	267	269	268	269	4	4
CFC-113	79	79	93	91	83	84	82	84	2	2
CH ₃ CCl ₃	139	139	173	194	149	156	147	150	7	12
CCl ₄	104	104	122	114	110	110	109	109	2	2
C ₂ Cl ₄	7	7	50	59	14	16	12	15	7	7
CHCl ₃	11	12	29	32	17	18	17	18	3	4
CH ₃ Cl	513	504	668	666	553	552	549	547	23	23
CH ₃ Br	8.6	8.6	18.3	22.3	10.6	11.4	10.4	11.0	1.3	2.0
CH ₃ I	0.1	0.3	1.3	2.0	0.3	0.6	0.3	0.6	0.1	0.2
Ethane	594	472	1725	1688	990	868	1000	817	235	249
Ethene	6	5	252	273	26	43	18	30	31	58
Ethyne	34	24	560	811	127	170	99	151	89	119
Propane	15	11	316	344	104	75	89	69	67	58
Propene	<DL	<DL	385	310	21	27	12	14	39	39
Propyne	<DL	<DL	43	112	5	9	<DL	4	9	14
n-Butane	<DL	<DL	90	128	20	23	10	11	21	31
i-Butane	<DL	<DL	56	70	11	15	6	6	12	20
n-Pentane	<DL	<DL	23	42	2	4	<DL	<DL	4	7
n-Hexane	<DL	<DL	24	25	<DL	<DL	<DL	<DL	2	3
Benzene	7	7	147	155	31	49	23	35	25	34
Toluene	<DL	<DL	86	189	15	24	12	19	12	21

s.d., standard deviation; <DL, below detection limit.

most strongly exhibited in missions 8 through 14, during which the highest MBL concentrations for C₂Cl₄, CH₃CCl₃, CFC-113, ethyne, benzene, and ozone were recorded. Missions 11 to 13 were the first three flights of the second Lagrangian experiment, which sampled the same air mass on consecutive flights [e.g., Wingenter *et al.*, this issue]. For these three missions, benzene was elevated by a factor of approximately 4 in the boundary layer compared to the free troposphere, and ethyne and C₂Cl₄ were enhanced by factors of 2. Back-trajectory analysis suggests that this air originated over England 2-4 days earlier [Bretherton and Pincus, 1995]. The vertical structure for mission 10 displayed in Figure 4 shows that, unlike subsequent missions, the hydrocarbon, C₂Cl₄, CFCs, CH₃Br, and ozone enhancements were most pronounced just above the boundary layer between 1000 and 2000 m (the layer is defined by the temperature inversion at about 1000 m for the first profile). This was typical for missions 8, 9, and 10. However, the MBL was more enhanced in the first profile than the second profile. Methyl iodide was elevated in both profiles but only in the MBL. Back-trajectories show that the polluted continental air sampled during missions 8-10 came from a more southerly region of Europe than encountered during missions 11-14, allowing the further

classification of these air masses as Continental European (Iberian), or Continental European (Northern).

Missions 8, 9, and 10 are shown in Figures 2 and 3 to have the greater concentration ranges for most species because they sampled clean Atlantic air and European outflow. Thus, in the following discussions of the predominant air mass types encountered, only samples representing the continental influence are included in the Continental (Iberian) classification. Box plots comparing the MBL concentration ranges for these two types of Continental European air masses are given in Figure 5, along with the ranges for two further air mass types described later. Figure 5 shows that the most noticeable difference in the chemical composition of the two European air masses is the significantly higher concentration of CH₃CCl₃ found in the northern case (missions 11-14). By contrast, the median concentrations of C₂Cl₄ and most of the hydrocarbons are slightly lower in the air from northern Europe. Methyl chloroform was widely used as a general purpose solvent, so the higher concentrations that appear to originate from this region are probably the consequence of different types of industrial use.

The lowest concentrations of most species were observed during the first Lagrangian series of flights, missions 5, 6, and

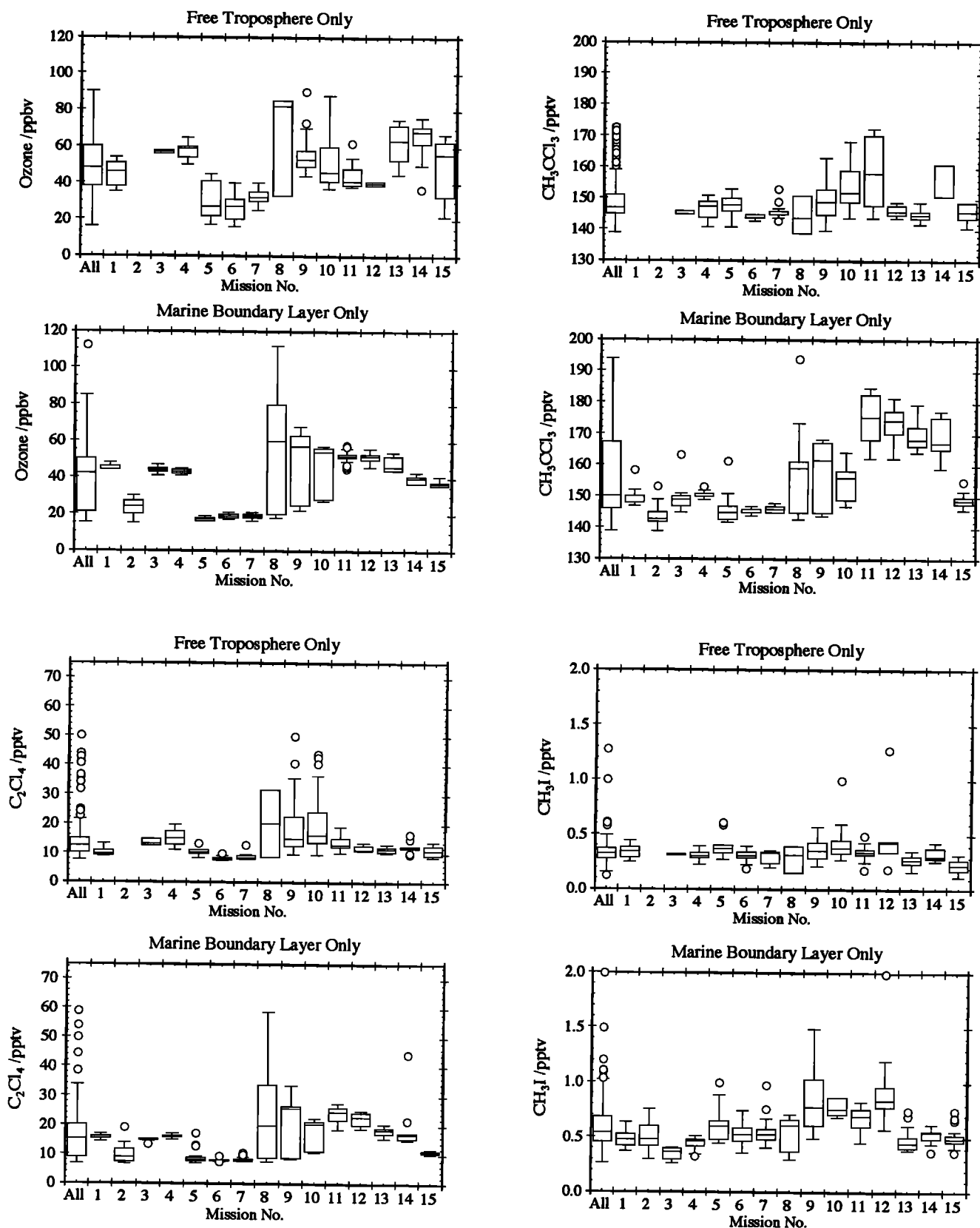


Figure 2. Free tropospheric and marine boundary layer box plot distributions of ozone, CH_3CCl_3 , C_2Cl_4 , and CH_3I for all missions and mission by mission. On these plot types the horizontal lines indicate the median values, the box encloses the upper and lower inner quartiles, and the lines extend over the data range or up to 1.5 times the inner interquartile distance. Individual points lying outside this range are indicated by open circles.

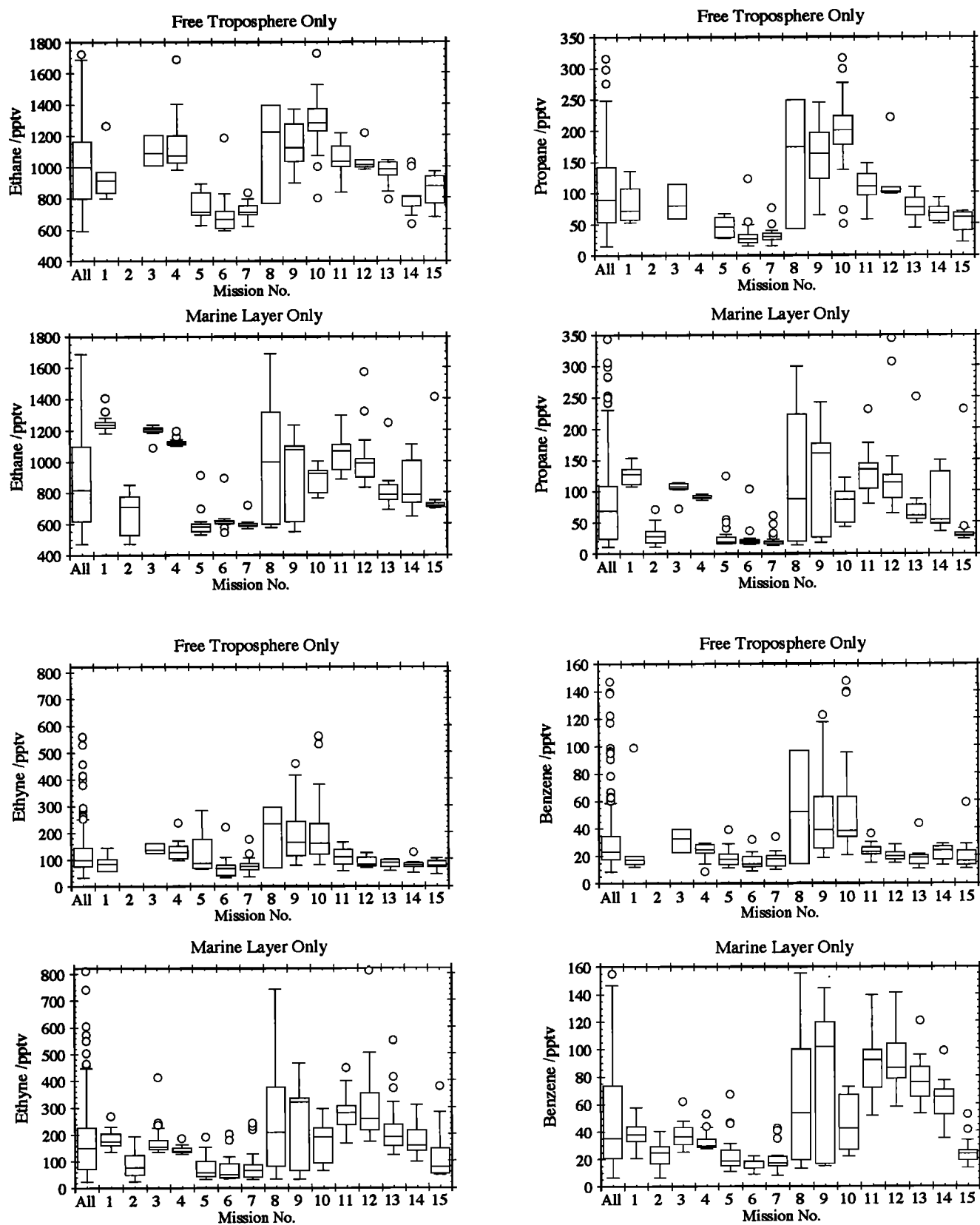


Figure 3. Free tropospheric and marine boundary layer mixing ratios of ethane, propane ethyne, and benzene for all missions and mission by mission. For a description of the plot type see Figure 2.

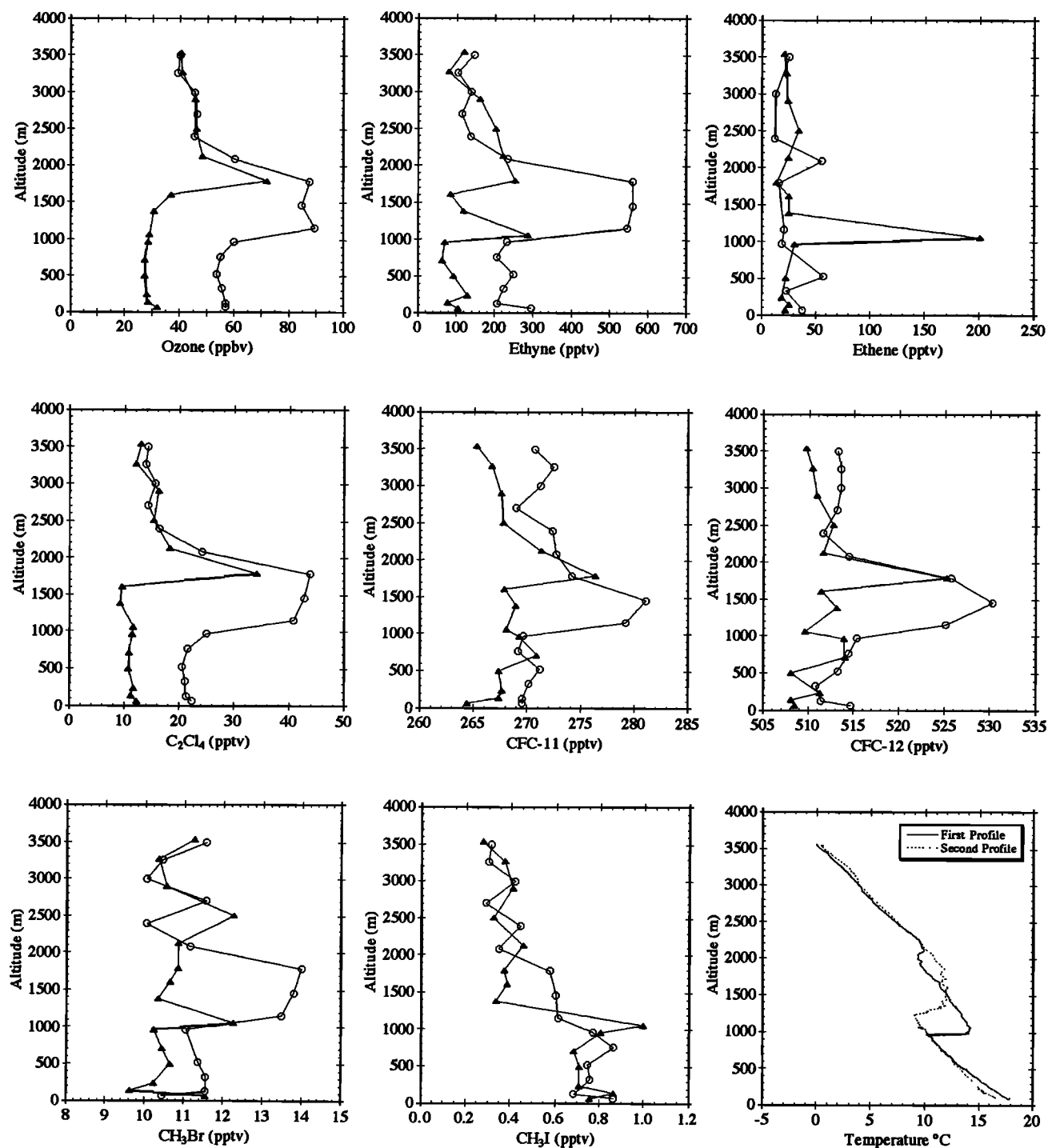


Figure 4. Vertical profiles of ozone, ethyne, ethene, C_2Cl_4 , CFC-11, CFC-12, CH_3Br , CH_3I , and temperature from mission 10 in air masses affected by European continental outflow. The open circles represent the first profile, made at 37.5-37.0°N, 25.0-24.3°W. The solid triangles represent the second profile, sampled at 38.2-39.0°N, 23.4-24.0°W.

7. They were made in clean Atlantic air associated with the strong high-pressure system near the Azores, and the air mass is labeled as clean marine in Table 1 and Figure 5. In general, the high-pressure system circulates air over the ocean, where it becomes well mixed and does not come into contact with land for many days. Consistent with this, the MBL was found to be chemically homogeneous. The shorter-lived anthropogenic

species n-butane, i-butane and n-pentane, whose lifetimes with respect to hydroxyl removal are approximately 1-3 days under summertime conditions, had decayed so that approximately 60%, 80%, and 90% of the samples, respectively, were below the 3 pptv detection limit. Figure 2 shows that ozone was also very low for these missions, further confirming that this was relatively pristine background air exhibiting very little impact

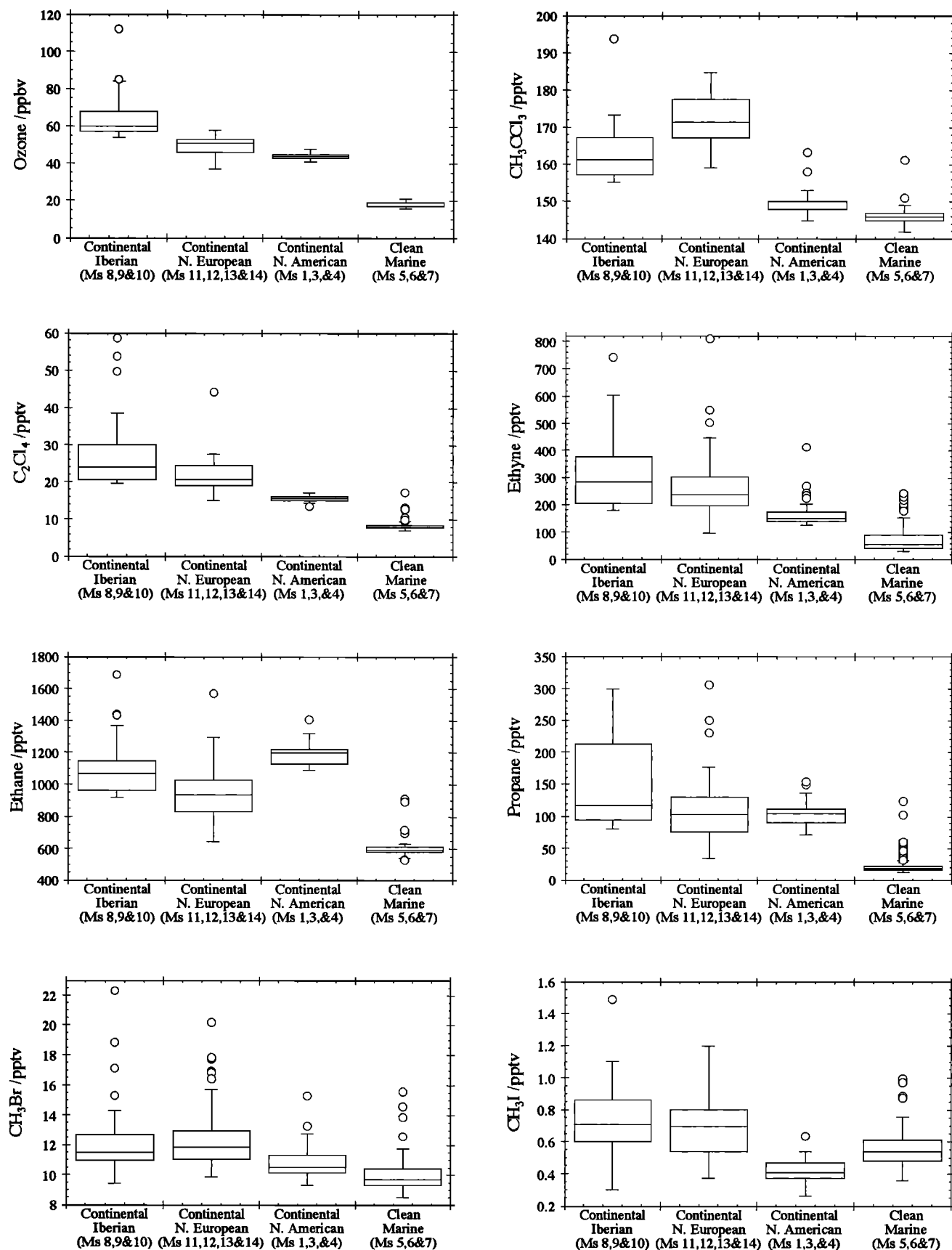


Figure 5. Box plot distributions of ozone, CH_3CCl_3 , C_2Cl_4 , ethyne, ethane, propane, CH_3Br , and CH_3I in the marine boundary layer for the four main air masses identified. For a description of the plot type, see Fig 2.

from continental emissions. The low concentrations of many components furnish useful comparisons for the continental air masses.

Even though wind directions during missions 1, 3, and 4 were similar to those experienced during missions 5, 6, and 7, the winds were lighter, and the area was under less influence from the strong surface high. Figures 2 and 3 show that the concentrations of ozone, C_2Cl_4 , ethane, ethyne, propane, and benzene were at least a factor of 2 higher than for the clean marine air. Ozone is a good indicator of aged continental pollution but can be perturbed by small additions of high-concentration stratospheric air, particularly at high altitude. Ethyne, benzene and C_2Cl_4 are more reliable indicators of relatively recent anthropogenic input. Ethyne and benzene are products of fossil fuel usage and have summertime atmospheric lifetimes of approximately 7 and 5 days, respectively, and C_2Cl_4 is a widely used solvent and degreasing agent with a 1-2 month summertime lifetime [Wang *et al.*, 1995]. These lifetimes are long enough to permit the detection of these species at a considerable distance from their sources, but short enough that the most recent emissions are significant and do not represent relatively small increments superimposed on high background concentrations, as is frequently the case for CFC compounds.

Five-day back-trajectory analysis suggests that the air encountered in missions 1, 3, and 4 had come from a westerly direction, with the North American continent being the probable source region. This conclusion is reinforced by the different characteristics exhibited by the results for missions 1, 3, and 4, compared to the continental air of European origin. For example, Figure 5 shows that the concentration of ethane in the MBL is significantly higher in this air mass than for the other three air masses shown. Trajectory analysis and the relatively low median concentrations of other pollutant gases (e.g., C_2Cl_4 and ethyne) compared to European outflow indicate that substantial dilution with clean marine air and photochemical aging must have taken place for at least 5 days. Figure 5 shows that for missions 1, 3, and 4 the median concentration of propane is also elevated relative to ethyne, even though propane is shorter lived than ethyne. In addition, the species ratios of both ethane and propane versus benzene in this air mass are 2-3 times as high as in the two other continental air masses studied. Ethane and propane are emitted as components of natural gas, which is their principal northern hemispheric source [Blake *et al.*, 1994]. Thus, relatively high mixing ratios of ethane and propane are consistent with natural gas emissions from North America making a characteristic impact on the air mass sampled in missions 1, 3, and 4.

Logarithmic ratios of the hydrocarbons in the different air masses also serve to differentiate them. Figures 6a and 6b are log-log plots for n-butane/ethane versus propane/ethane and the i-butane/ethane versus n-butane/ethane concentrations, respectively, for the four predominant air masses. Plots similar to these have been employed by several research groups [e.g., Rudolph and Johnen, 1990; Parrish *et al.*, 1992; Finlayson-Pitts, 1993; McKeen and Liu, 1993; Jobson *et al.*, 1994] to gain insight into the sources, photochemical removal processes and atmospheric mixing of hydrocarbon and halocarbon gases.

The least-squares fit through the n-butane/ethane versus propane/ethane plot in Figure 6a gives a slope of approximately 1.60 ($R^2 = 0.63$). This is slightly higher than the results shown by Parrish *et al.* [1992], who reported a slope of 1.47 ($R^2 = 0.89$) for a wide range of northern hemispheric measurements, including Pacific Ocean and urban values. Rudolph and Johnen

[1990] reported a slope of 1.66 ($R^2 = 0.71$) for the Atlantic between 50°N and 40°S during March and April. Parrish *et al.* calculated a slope of 2.77 from the relative rates of reaction of HO with the various hydrocarbons, and argued that the difference between calculation and observations is the consequence of dilution by air masses of different photochemical ages.

As discussed by Parrish *et al.*, Figure 6a shows that samples with the most recent anthropogenic input have higher n-butane/ethane and propane/ethane ratios, while those measured in the clean marine atmosphere tend to have the lowest ratios. This is expected if the initial ratios are all similar and prolonged exposure preferentially removes the more reactive components. However, it is interesting that the values for the continental air mass of North American origin appear to form a distinct group below the least squares fit line to all the data, with n-butane/ethane ratios as low as the lowest clean marine samples but propane/ethane ratios in the same range as the other two continental air masses. The small range covered by the Continental (North American) data is remarkable, considering that the samples were collected on three different days nearly a week apart. The low n-butane/ethane concentration ratio for these measurements is most likely to have been caused by the significantly larger contribution from natural gas and the longer transit time from North America to the sampling location. However in many cases the European influenced samples were enhanced in n-butane. This is most likely the result of reduced transport time to the experimental region and extensive use throughout Europe of liquified petroleum gas which is composed mainly of propane and butanes (Blake and Rowland, 1995). A similar effect is seen in Figure 6b for i-butane/ethane versus n-butane/ethane. The least-squares fit through the i-butane/ethane versus n-butane/ethane plot gives a slope of approximately 0.98, which is consistent with previous measurements [Jobson *et al.*, 1994]. Both n-butane and i-butane have similar sources, and the rate of reaction of n-butane with HO is only 10% faster than for i-butane [Atkinson, 1990]. Therefore, the samples from missions 1, 3 and 4 now provide the lowest ratios on both axes and follow the least-squares fit through the points from the other three air masses. In summary, even though previous comparisons have found remarkably good agreement between hydrocarbon ratios from different air masses, this work emphasizes that the strictly linear relationships and photochemical age progression discussed by, e.g., Parrish *et al.* [1992], are sensitive to the basic assumption that the air masses have similar initial compositions.

Ethane and propane have slightly higher mean concentrations in the free troposphere than in the MBL (Table 2). Figure 3 shows that this trend is particularly apparent for missions 5, 6, and 7, the clean marine Lagrangian series of flights. Figure 7 includes the vertical distribution of ethane and ozone for these three flights, and shows that above about 1000 m both of these gases were significantly enhanced. The low concentrations of shorter-lived gases such as ethyne (see Figure 7), n-butane, and n-pentane showed relatively little recent continental influence. Trajectory analysis suggests that at higher altitudes in the free troposphere, missions 5, 6, and 7 may have had some influence from air of North American origin. It has been seen that the flights most likely to characterize emissions from North America (1, 3, and 4) also exhibited particularly high ethane and propane mixing ratios. Thus the relatively high concentrations of ethane and propane observed in the free troposphere for missions 5, 6, and 7 are consistent with some mixing with air of North American origin.

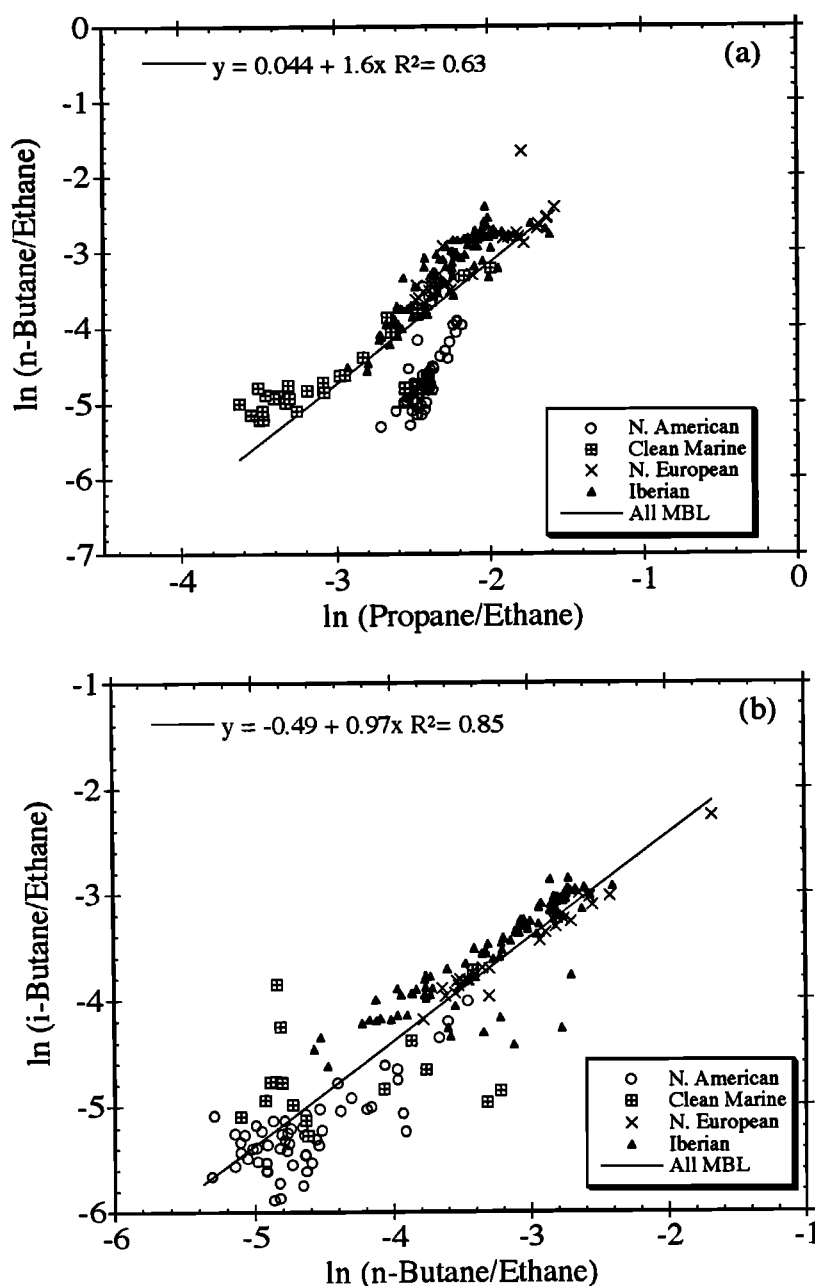


Figure 6. Plot of the logarithm of the concentration ratios (a) n-butane/ethane versus propane/ethane and (b) i-butane/ethane versus n-butane/ethane in the marine boundary layer for the four predominant air masses identified during ASTEX/MAGE.

Figure 7 (missions 5, 6, and 7) shows that the MBL ozone is only about half the FT value. This is consistent with a high-altitude stratospheric ozone source and a low-altitude sink. At low altitudes the relatively high moisture associated with clean MBL air is expected to produce net photochemical ozone loss during daylight under low NO_x conditions. However, Table 2 shows that the median ozone in the MBL was only slightly lower than for the FT. This reflects the prevalence of photochemical ozone production in the MBL caused by low-altitude European continental outflow into the NE Atlantic.

Most of the long-lived halocarbon gases (e.g., CFC-12, CFC-11, and CCl_4) have similar mixing ratios in the free troposphere and MBL. These gases tend to have relatively high background

mixing ratios and are regulated by the Montreal Protocol because of the effect of their decomposition products on stratospheric ozone. Thus their usage in most urban areas had already begun to decline, and they are no longer expected to be particularly good markers for urban influence on air masses. It is interesting then that the vertical profiles made during mission 10 sampled an urban plume between 1000 and 2000 m that was not only enhanced in gases typical of urban emissions such as C_2Cl_4 , CH_3CCl_3 , CFC-113, ethyne, and benzene, but was also significantly enhanced in CFC-11 and CFC-12 (see Figure 4). This is consistent with the results of *Simmonds et al.* [1993], who analyzed air over Ireland with European trajectories and reported evidence of declining but still significant CFC-11 and

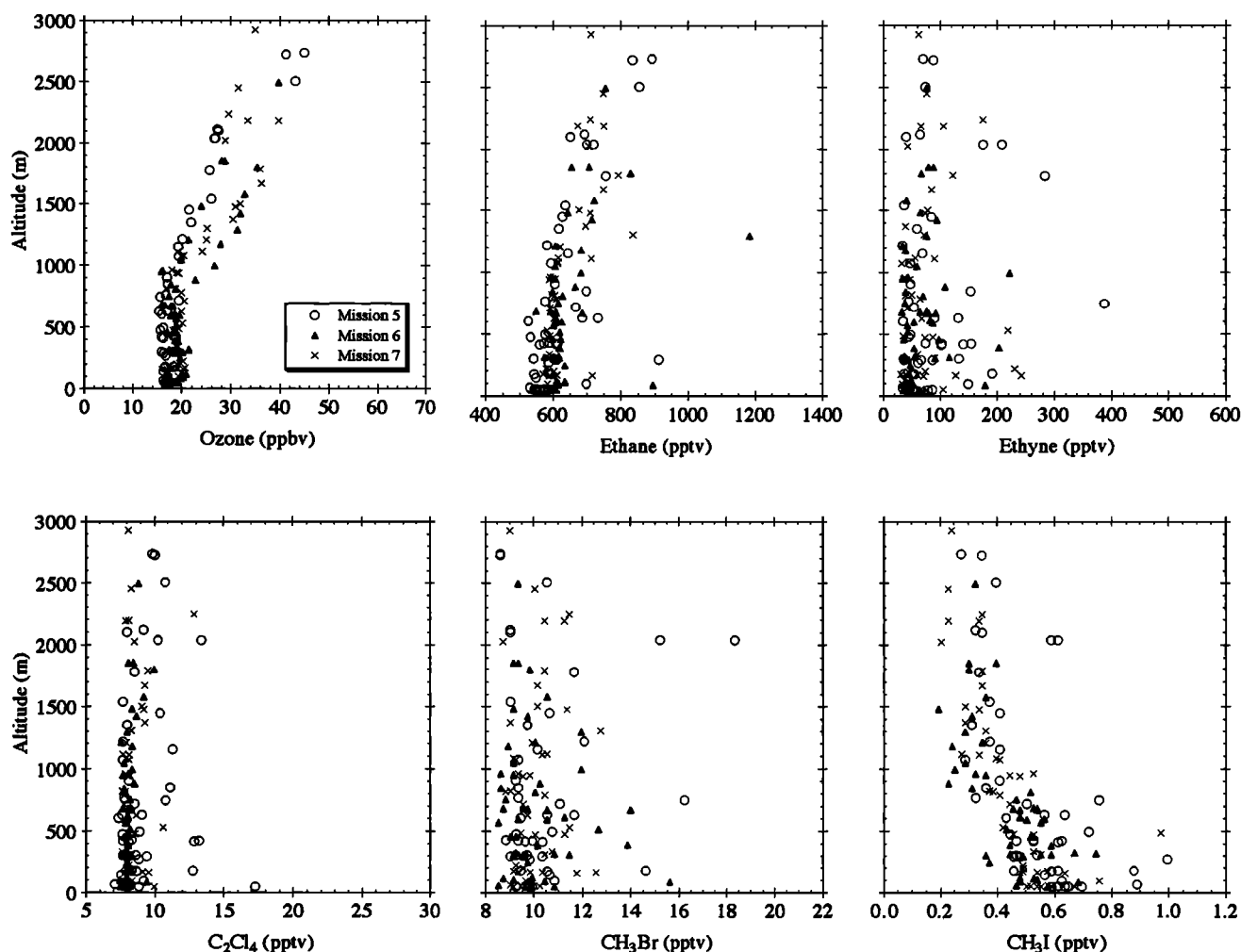


Figure 7. Vertical distribution of ozone, ethane, ethyne, C_2Cl_4 , CH_3Br , and CH_3I for all samples collected during missions 5, 6, and 7 (June 12 and 13, 1992).

CFC-12 emissions from Europe during 1987-1990. Figure 4 also shows that this layer contained enhanced methyl bromide concentrations, supporting reports of continental sources for this gas which include agricultural [Yagi *et al.*, 1995] and domestic fumigation and leaded gasoline [Baumann and Heumann, 1987]. No specific trajectory analysis is available, but the meteorological analysis suggests that this tongue of continental air had moved into the area from the Iberian Peninsula [Bretherton and Pincus, 1994]. The same aerosol-rich air mass was sampled the previous day when there was evidence of similar gas enhancement between 1000 and 1500 m.

Ethene and propene are significantly elevated in the MBL (see Table 2) but do not show significant enhancements in either continental air or in urban plumes (e.g., see ethene in Figure 4). These gases are known to have large urban sources [Singh and Zimmerman, 1992] but are too short lived (atmospheric lifetimes less than 1 day) to have been transported from the continents into the ASTEX/MAGE area. They have been reported to have significant oceanic sources, which likely contributed to the MBL enhancement [Donahue and Prinn, 1990; Rudolph and Johnen, 1990]. However, the profile in Figure 4 shows an example of one of the ethene-enhanced samples or "spikes" which were regularly observed. These spikes were not enhanced in any of the

other measured gases except for propene, or occasionally ethyne, which is a good indicator of combustion. These spikes of relatively freshly emitted material may therefore have originated from commercial aircraft and/or ships in the area, or those taking part in the experiment. Such problems were particularly apparent in the clean marine first Lagrangian experiment, during missions 5 and 6 which saw intensive use of ship and aircraft sampling platforms, with large spikes superimposed on a very low background.

Mixing ratios of CH_3I in the MBL are approximately double those in the FT (see Table 2). For comparison, Table 2 shows CH_3Br to be enhanced by approximately 5% in the MBL. Figure 5 shows that both halocarbon gases are significantly elevated in air with European continental back-trajectories, with methyl iodide being enhanced by about 30% above clean marine conditions, and methyl bromide by about 20%. However, methyl iodide exhibits less correlation with urban gases in the individual continental European plumes than methyl bromide (see Figure 4). This evidence suggests that a significant component of the methyl bromide may originate from urban areas. It is also consistent with the area to the east of the Azores being particularly rich in nonurban methyl iodide sources. The vertical profiles shown in Figure 7 for the clean marine missions (5, 6,

and 7) reveal particularly strong MBL enhancements for methyl iodide, further implying an oceanic source. Eighty surface samples were collected at different locations and elevations on the Islands of Santa Maria and São Miguel. All island samples exhibited elevated levels of CH_3I with some being an order of magnitude higher than the 0.6 pptv mean boundary layer value given in Table 2. In addition, concentrations of many other halogenated gases other than CH_3Br were substantially elevated in the island samples. These airborne and island observations are consistent with previous work showing higher concentrations of CH_3I in North Atlantic coastal waters [Moore and Tokarczyk 1993] and on the English coast in air from the Atlantic [Oram and Penkett, 1994]. Strong convective events are able to rapidly transport this CH_3I to the upper troposphere and even the lower stratosphere, particularly in the tropics [Pickering et al., 1992; Kritiz et al., 1993]. It has been suggested [Solomon et al., 1994] that short-lived iodine containing gases could play a role in ozone depletion in the tropical lower stratosphere.

Conclusion

During ASTEX/MAGE, circulation patterns resulted in the transport of continental air from North America and Europe to the NE Atlantic. Each of these air masses was characterized by its distinctive halocarbon and hydrocarbon composition. The continental air from both North America and Europe was enriched in hydrocarbon and halocarbon photochemical ozone precursors and ozone, suggesting that photochemical production from emissions originating from both continents contribute to the summertime tropospheric ozone budget in the Atlantic region. European influence resulted in preferentially enhanced MBL concentrations of many anthropogenic hydrocarbons, halocarbons, and ozone. Longer range transport from North America was associated with a more even distribution of pollutants between the free troposphere and MBL. Industrially emitted gases and solvents were used effectively to verify calculated trajectories. Methyl iodide and methyl bromide concentrations were enhanced in the MBL and in air with European trajectories, with some evidence of the influence of anthropogenic/urban sources for methyl bromide. The distribution of methyl iodide, however, was more consistent with oceanic and, in particular, coastal sources playing a dominant role.

Acknowledgments. The authors thank the following for their support during the field mission: John Bilicska, Sonna Bristle, George Bonne, Barbara Chisholm, Nancy Coneybeare, Murray McEachern, Ralph Kolbush, Alan Potts, Barkley Sive, Pam Sullivan and Phred Weinert. We especially thank George Harvey of the NOAA/AMOL Facility in Miami, Florida, for the use of his laboratory and for his support of our field analytical system. We also thank Brad Berger for providing plots and merged data sets and Greg Kok and Richard Schillawski for the ozone data. This work was supported by funds from the National Science Foundation (NSF) grant ATM-9121739.

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D.R. Blake, N.J. Blake, O.W. Wingenter, and F.S. Rowland, Department of Chemistry, University of California, Irvine, CA 92717. (e-mail: dblake@orion.oac.uci.edu; nblake@orion.oac.uci.edu; owwingen@orion.oac.uci.edu; rowland@uci.edu)

T.W. Smith Jr., National Center for Atmospheric Research, P.O. Box 3000, Boulder, Colorado 80307-3000. (e-mail: ty@terra.colorado.edu)

(Received October 7, 1994; revised March 4, 1995; accepted March 4, 1995.)